

Supporting Information

For

Tracking the Adsorption and Electron Injection Rates of CdSe
Quantum Dots on TiO₂: Linked Versus Direct Attachment

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Section S1. Effect of Washing on QD Size Distribution

Figure S1 shows negligible changes to the absorbance spectra of toluene-suspended QDs following successive wash cycles. These spectra give evidence that the particle size distribution remains largely unchanged after washing.

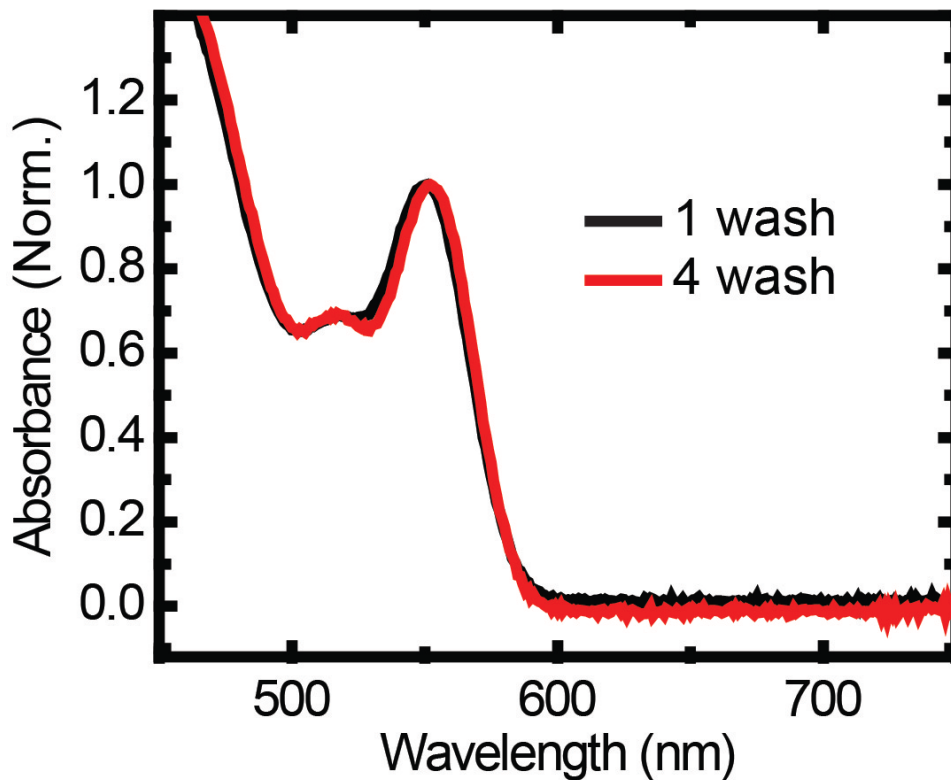


Figure S1. Absorbance spectra for CdSe QDs washed with the procedure described in the main text once and four times. The negligible difference between the spectra demonstrates the absence of QD sample size alteration via washing.

Section S2. Derivation for QDs Adsorbed Per TiO₂ Nanoparticle

Figures 3 and S2 as well as the data in Table 2 show adsorption normalized to the amount of TiO₂ in the optical cell. Rather than normalize the data to TiO₂'s mass, we chose to normalize the data in a more physically insightful way. In these figures we divide the number of QDs adsorbed by the number of TiO₂ nanoparticles.

Equation S1 relates the mass of TiO₂ to the number of TiO₂ nanoparticles in the system

$$NP_{TiO_2} = \frac{m}{\rho V_{TiO_2}} \quad (S1)$$

where NP_{TiO_2} is the number of TiO₂ nanoparticles, m is the mass of TiO₂, ρ is the density of TiO₂, and V_{TiO_2} is volume per TiO₂ particle. Assuming spherical nanoparticles, Equation S2 then follows

$$NP_{TiO_2} = \frac{m}{\rho \left(\frac{4}{3}\right) \pi r^3} \quad (S2)$$

where r is the particle radius. ρ was taken to be 3.84 g cm⁻³ for anatase TiO₂, and r equals 10 nm for Dyesol 90T TiO₂ paste. Equation S3 (the same as main article Equation 1) relates the number of particles that adsorb onto TiO₂ to the absorbance values from the UV-Visible spectrophotometer.

$$QD_{ads} = \left(\frac{A_0 - A_t}{\epsilon l} \right) N_A V_{sol} \quad (S3)$$

Here, QD_{ads} represents the number of QDs that have adsorbed onto TiO₂, A_0 is the initial absorbance value, A_t is the absorbance value at a given measurement time, ϵ is the QD solution's tabulated molar absorptivity, N_A is Avogadro's number, l is the path length (1cm)

and V_{sol} is the volume of the solution (2.4 mL). Dividing Equation S3 by Equation S2 then results in the parameter of interest, the number of QDs adsorbed per TiO_2 nanoparticle.

$$\frac{QD_{ads}}{NP_{TiO_2}} = \frac{(A_0 - A_t)N_A V_{sol} \rho \left(\frac{4}{3}\right) \pi r^3}{m \epsilon l} \quad (S4)$$

An example of the practical nature of using the calculation from Equation S4 to plot the increased loading of CdSe QDs onto a nanostructured TiO_2 film is shown in Figure S2, which demonstrates the effect of washing on directly adsorbed quantum dots. Subsequent washes with methanol results in a greater number of particles adsorbing onto TiO_2 .

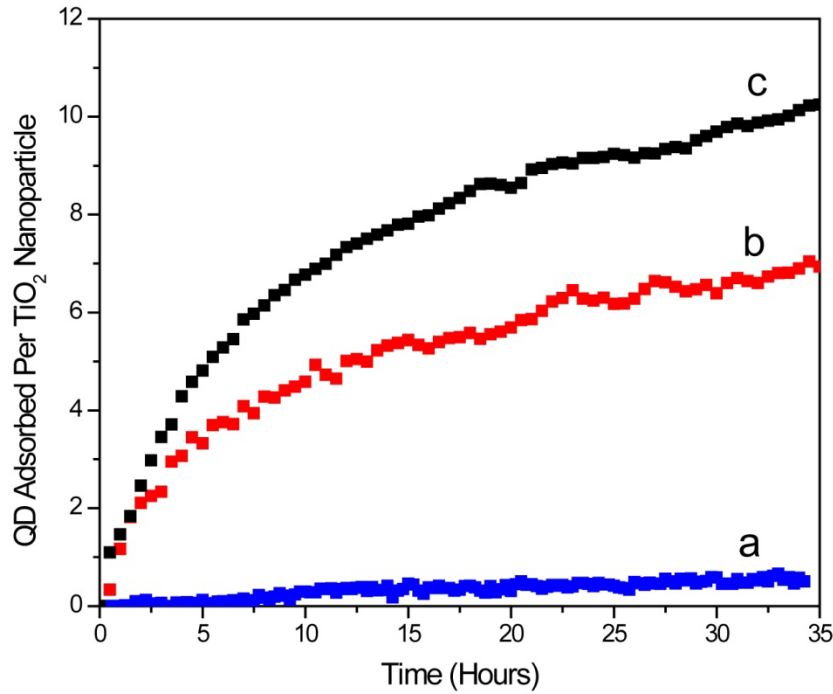


Figure S2. Time dependent CdSe QD adsorption onto TiO_2 with QDs washed (a) once, (b) thrice, and (c) five times with methanol. Traces represent directly adsorbed, 2.6 nm average diameter QDs at a concentration of 9.5 μM . Direct comparison should not be made with main article Figure 3 due to size and concentration differences, although the same trend between number of washes and adsorption onto TiO_2 was observed.

Section S3. Additional Information for the Kinetic Adsorption Model

Detailed Kinetic Adsorption Model. Equation S5 (the same as Equation 8 from the main article) is the basis for Langmuir-like monolayer adsorption of CdSe QDs on TiO₂, relating the decrease in QD concentration in solution to pseudo-first order adsorption and first order desorption of QDs.

$$\frac{-d[P]_{Lang}}{dt} = k_1'[P] - k_{-1}[PS] \quad (S5)$$

Here, $P(t)_{Lang}$ refers to the particles that leave toluene and adsorb as a sub-monolayer on TiO₂, P is the concentration of QDs in solution and PS is the concentration of QDs adsorbed to TiO₂. PS is then related to the original concentration of QDs in solution,

$$PS = P_0 - P \quad (S6)$$

resulting in

$$\frac{-d[P]_{Lang}}{dt} = k_1'[P] - k_{-1}[P_0 - P] \quad (S7)$$

which is only a function of P . Integration then results in Equation S8, which is the expression that was used to model sub-monolayer adsorption.

$$[P(t)]_{Lang} = [P_0] - \left(\frac{k_1'[P_0]e^{-(k_1' + k_{-1})t} + k_{-1}[P_0]}{k_1' + k_{-1}} \right) \quad (S8)$$

The negative sign in front of Equations S5 and S7 drops because Equation S8 considers the TiO₂ reference frame rather than the QD solution reference frame.

Experimental deviation from Equation S8 is attributed to QD aggregation onto already-adsorbed QDs and is modeled by Equation S9 (the same as main article Equation 9):

$$\frac{-d[P]_{ag}}{dt} = k_{ag}[P][P_nS] \quad (S9)$$

where P_nS represents any number of particles adsorbed onto a TiO_2 site. A reverse aggregation process likely occurs, but its rate was assumed to be sufficiently small as to be ignored. Using the trapezoid method of approximate integration on Equation S9 results in the following:

$$[P(t)]_{ag} = [P]_{ag,t-1} + k_{ag}[P]_{t-1}[P_nS]_{t-1}\Delta t \quad (S10)$$

where Δt is the time difference between measurements and $t-1$ refers to the time of the measurement previous to the time of the data point of interest. P is the number of CdSe particles in solution, P_nS refers to any number of particles adsorbed or aggregated onto individual TiO_2 adsorption sites, and P_{ag} is the total number of particle aggregates across all TiO_2 adsorption sites. The overall adsorption model consists of the sum of Equations S8 and S10:

$$[P(t)]_{total} = [P(t)]_{Lang} + [P(t)]_{ag}. \quad (S11)$$

Constants k_1' , k_{-1} , and k_{ag} were iterated upon until the sum of the squared error between the model and experimental data was minimized.

The model presented here is a fairly simple one, with its inherent limitations and significant room for improvement. First, the de-aggregation rate was assumed to be negligible. Incorporation of a de-aggregation rate could give additional insights to the adsorption process while adding a degree of complexity to the model. Second, sub-

monolayer adsorption was modeled with a separate equation from that of aggregation. As more particles aggregate, the concentration of QDs in solution decreases. This process should then cause some singly adsorbed QDs to desorb back into toluene to maintain equilibrium. Because monolayer adsorption and aggregation were considered in separate equations, the effects of aggregation were not felt by the model's singly adsorbed QDs. The error introduced here is relatively small for the 48-hour timescales used in this investigation, but as adsorption time continues to increase, more and more particle aggregation will occur and the error due to this assumption will become more significant. Third, the model did not account for differences for varying numbers of QDs aggregated on the same TiO_2 site. A larger agglomeration of particles should have a greater statistical likelihood of attracting a QD in solution to aggregate there. Once again, these effects are not strongly pronounced for short (<48 hours) adsorption times.

Expression for Percent Coverage of TiO_2 . The fractional coverage of CdSe QDs on TiO_2 was determined by a simple relation between the number of available TiO_2 sites (see following sub-section entitled “Expression for Number of Available TiO_2 Adsorption Sites” for explanation and expression) and the number of particles adsorbed on TiO_2 . This parameter was used to justify the assertion that forward, sub-monolayer adsorption process can be expressed with a pseudo first order adsorption rate. If the fractional coverage is sufficiently low, this assertion is justified. As such, Equation S12 takes into account a case of maximal QD coverage: that is, how much of TiO_2 's available surface area would be covered by QDs if all adsorbed particles formed a sub-monolayer. For reasons discussed in the main article, an assumption of purely sub-monolayer coverage is incorrect.

However, here this assumption allows for a worst-case scenario for determining if forward adsorption may be simplified to a pseudo first order adsorption rate.

$$\% Coverage = \frac{QD_{ads}}{S_0} \times 100\% = \frac{\left(\frac{A_0 - A_t}{\epsilon l}\right) N_A V_{sol}}{S_0} \times 100\% \quad (S12)$$

Through use of this equation, a maximum coverage of less than 10 percent was obtained after 48 hours for most adsorption experiments.

Expression for Number of Available TiO₂ Adsorption Sites. Use of several equations in the kinetic model required knowledge of S_0 , the maximum number of TiO₂ adsorption sites. This maximum number of sites was estimated under the assumption of a close-packed monolayer of QDs on TiO₂. TiO₂'s total surface area per unit mass was divided by the cross-sectional area of one QD particle and multiplied by 0.9069, the packing limit for circles on a two dimensional surface. This expression was then multiplied by the mass of TiO₂ to obtain the number of available adsorption sites S_0 , seen in Equation S13.

$$S_0 = (0.9069) \frac{SA_{TiO_2} m_{TiO_2}}{\pi (r_{CdSe})^2} \quad (S13)$$

The surface area of TiO₂ was taken to be 65.4 m² g⁻¹, the average of the literature's reported values for Dyesol TiO₂ paste with average particle diameter 20 nm.^{1,2} The addition of MPA was assumed to have a negligible impact on the number of available adsorption sites.

Section S4. Summary of Points for Improved QD Adsorption on TiO₂

Storage. Keeping TOPO-capped QDs in an inert environment is necessary for them to remain stable (suspended) in toluene. If exposed to atmospheric oxygen, QDs will flocculate out of toluene within days. For the same reason, nitrogen-purged toluene is used in all steps of the preparation and adsorption processes.

QD Washing. Washing the QDs with methanol prior to adsorption has a significant impact on how well they adsorb onto TiO₂. This process removes TOPO from the QD surface and improves the affinity of QDs for TiO₂ and MPA. After five washes, the QDs begin to lose stability in toluene as sub-critical amounts of TOPO cause QD aggregation.

MPA-Assisted Adsorption Steps. It is necessary that fresh, anhydrous acetonitrile be used in the preparation of the MPA solution and in the rinsing steps outlined in the main article's experimental section. The rinsing steps ensure that no unanchored MPA molecules are introduced to the CdSe-toluene mixture, where they can bind to CdSe and reduce the suspension's stability.

Use of MPA. Using MPA to assist in adsorption results in more particles adsorbing onto TiO₂ compared to direct adsorption. However, QDs bound to TiO₂ through MPA experience slower electron injection into TiO₂, as discussed in the main article. This consequence should be kept in mind when using linker-assisted adsorption for photovoltaic devices.

Concentration Dependence. Adsorption occurs through an equilibrium process. As such, a greater concentration of QDs in solution will yield a greater number of QDs adsorbing onto TiO₂.

Supporting Information References

- (1) Kim, Y. J.; Lee, M. H.; Kim, H. J.; Lim, G.; Choi, Y. S. et. Al. *Adv. Mater.* **2009**, *21*, 3668.
- (2) Docampo, P.; Guldin, S.; Stefiak, M.; Tiwana, P.; Orilall, M. C. et. Al. *Adv. Funct. Mater.* **2010**, *20*, 1787.